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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

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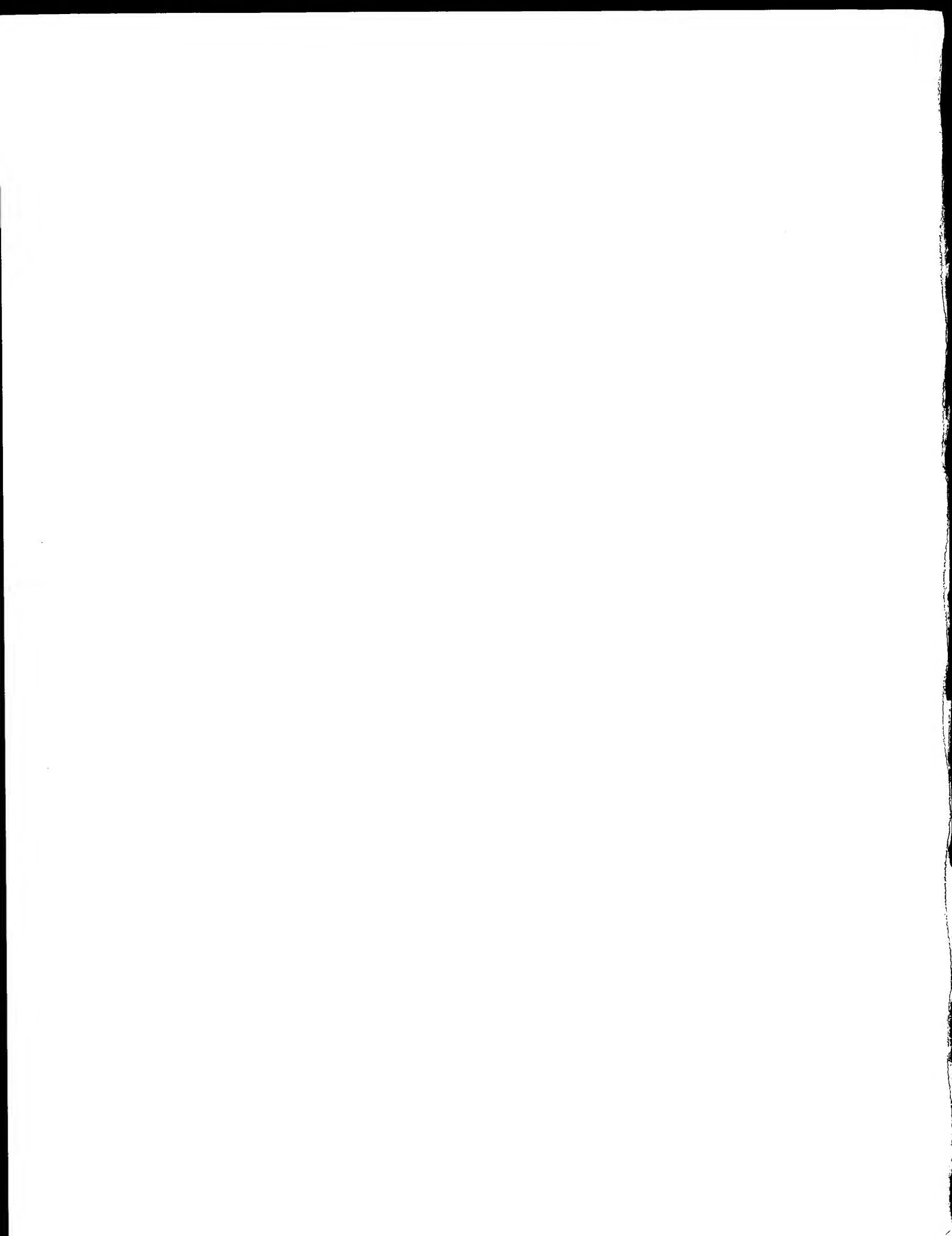
Der Präsident des Europäischen Patentamts;
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For the President of the European Patent Office

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Sheet 2 of the certificate
Page 2 de l'attestation

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Process for sizing paper

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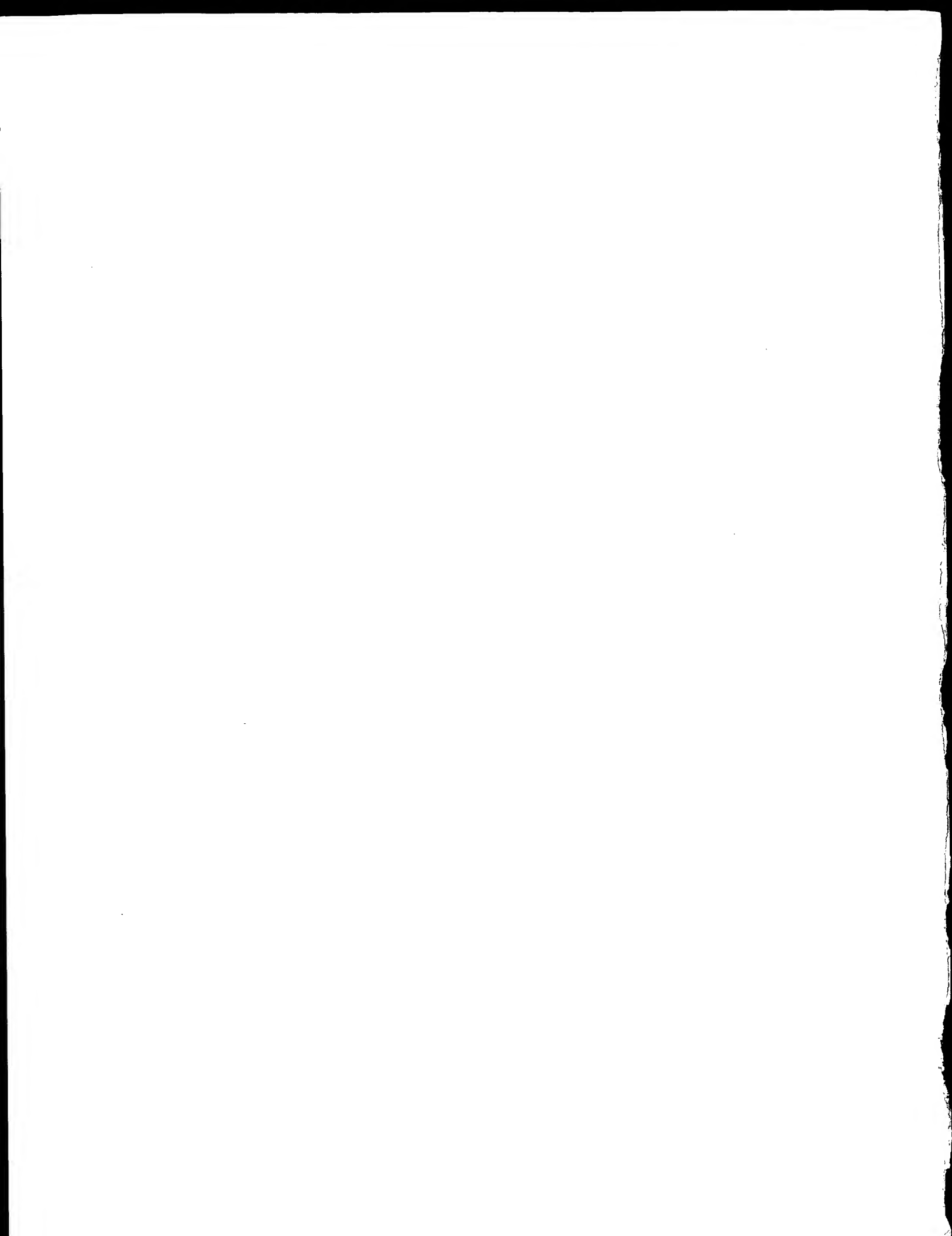
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Process for sizing paper

The present invention refers to a process for sizing paper comprising adding to a suspension an anionic or cationic sizing dispersion and a sizing promoter wherein the sizing promoter comprises an anionic polymer (a) containing at least one aromatic group.

5 Background

Dispersions or emulsions of sizing agents are used in papermaking in order to give paper and paper board improved resistance to wetting and penetration by various liquids. The sizing dispersions are usually added to an aqueous suspension containing cellulosic fibres, optional fillers and various additives. The aqueous suspension is fed into
10 a headbox ejecting the suspension onto a wire where a wet web of paper is formed. To the suspension is further commonly added compounds such as starches and microparticulate materials which facilitate the dewatering of the suspension on the wire. The water drained from the wire, referred to as white water, is usually partly recirculated in the papermaking process. The cellulosic suspension contains a certain amount of non-
15 fibrous material, for example fillers, charged polymers, sizing agents and various charged contaminants, i.e. anionic trash, electrolytes, colloidal substances, etc.. The non-fibrous material has an influence on the sizing efficiency and commonly impairs the sizing efficiency. High amounts of charged compounds such as high contents of salts in the suspension renders a suspension which is increasingly difficult to size, i.e. to obtain a
20 paper with satisfactory sizing properties. Other compounds contained in the suspension which deteriorates sizing are various lipophilic wood extractives which may come from recycled fibres and mechanical pulps. An increased amount of added sizing agent often improve sizing, however, leading to higher costs as well an increased accumulation of sizing agents in the white water. The accumulation of non-fibrous material as well as any
25 other component present in the suspension will be even more pronounced in mills where white water is extensively recirculated with the introduction of only low amounts of fresh water into the papermaking process. Thus, it is an objective of the present invention to further improve sizing. Another objective of the present invention is to improve sizing when applying sizes on cellulosic suspensions having high conductivities. Yet further
30 objectives will appear hereinafter.

US 5595629 discloses a paper making process comprising forming an aqueous cellulosic paper making slurry and adding a cationic polymer and an anionic polymer to the slurry to increase retention and/or drainage. The anionic polymer comprises a formaldehyde condensate of a naphthalene sulfonic acid salt.

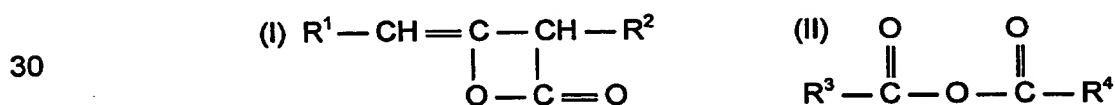
35 Invention

It has been found that the invention according to the claims surprisingly solves the problems outlined in the application. More specifically, the invention relates to a

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process for sizing paper comprising adding to a suspension an anionic or cationic sizing dispersion and a sizing promoter wherein the sizing promoter comprises an anionic polymer (a) and optionally a polymer (b), whereby polymer (a) and (b) contain at least one aromatic group each.

- 5 The anionic or cationic sizing dispersion added to the suspension comprises suitably any sizing agent known, such as non-cellulose-reactive agents including rosins, e.g. fortified and/or esterified rosins, waxes, fatty acids and resin acid derivatives, e.g. fatty amides and fatty esters, e.g. glycerol triesters of natural fatty acids, and/or cellulose-reactive agents. Preferably, the sizing dispersion contains at least one cellulose-reactive
- 10 sizing agent. The cellulose-reactive sizing agents comprised in the sizing dispersion can be selected from any cellulose-reactive agents known in the art. Suitably, the sizing agent is selected from the group consisting of hydrophobic ketene dimers, ketene multimers, acid anhydrides, organic isocyanates, carbamoyl chlorides and mixtures thereof, preferably ketene dimers and acid anhydrides, most preferably ketene dimers. Suitable ketene dimers
- 15 have the general formula (I) below, wherein R^1 and R^2 represent saturated or unsaturated hydrocarbon groups, usually saturated hydrocarbons, the hydrocarbon groups suitably having from 8 to 36 carbon atoms, usually being straight or branched chain alkyl groups having 12 to 20 carbon atoms, such as hexadecyl and octadecyl groups. In a preferred embodiment, the ketene dimers are liquid at ambient temperature, i.e. at 25 °C, suitably at
- 20 20 °C. Suitable acid anhydrides can be characterized by the general formula (II) below, wherein R^3 and R^4 can be identical or different and represent saturated or unsaturated hydrocarbon groups suitably containing from 8 to 30 carbon atoms, or R^3 and R^4 together with the -C-O-C- moiety can form a 5 to 6 membered ring, optionally being further substituted with hydrocarbon groups containing up to 30 carbon atoms. Examples of acid anhy-
- 25 drides which are used commercially include alkyl and alkenyl succinic anhydrides and particularly isooctadecenyl succinic anhydride.



- Suitable ketene dimers, acid anhydrides and organic isocyanates include the
- 35 compounds disclosed in U.S. Pat. No. 4,522,686, which is hereby incorporated herein by reference. Examples of suitable carbamoyl chlorides include those disclosed in U.S. Pat. No. 3,887,427 which is also incorporated herein by reference.

The anionic or cationic sizing dispersion may also comprise a polymer (c) containing at least one aromatic group.

In accordance with the present invention an anionic or cationic sizing dispersion and a sizing promoter comprising an anionic polymer (a) containing at least one aromatic group and optionally a polymer (b) containing at least one aromatic group is(are) added to a suspension containing cellulosic fibres. The anionic polymer, i.e. having an overall
5 anionic charge, preferably is an organic polymer and may be water-soluble or water-dispersable. The anionic polymer (a) can be linear or branched. Suitably, the aromatic group of the anionic polymer can be present in the polymer backbone or, preferably, it can be a pendant group attached to or extending from the polymer backbone or be present in a pendant group that is attached to or extending from the polymer backbone (main chain). The
10 anionic polymer (a) has suitably at least one aromatic group and at least one anionic group such as a sulphonate, phosphate, phosphonate, sulphate or carboxylic acid group which can be attached directly to an aromatic group or be attached to a chain of atoms which in turn is attached to the aromatic group. Suitable anionic polymers include condensated naphthalene sulphonates, polystyrene sulphonates and lignosulphonate.

15 According to one preferred embodiment of the present invention the sizing promoter comprises a further polymer (b) containing at least one aromatic group. Polymer (b) is suitably cationic or amphoteric, i.e. having an overall cationic charge, and may be referred to as a polyelectrolyte. Polymer (b) may be derived from natural sources or can be a synthetic polymer selected from homopolymers and copolymers prepared from one or
20 more monomers comprising at least one monomer having an aromatic group, thus, polymer (b) is preferably an organic polymer.

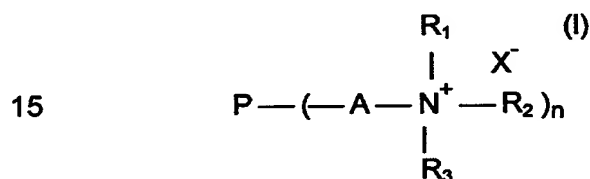
Polymer (b) can be a polysaccharide containing at least one aromatic group and may be cationic or amphoteric, i.e. containing at least one aromatic group and one or more cationic groups, the cationic groups being suitably tertiary or quaternary ammonium groups.
25 The polysaccharide may also contain one or more anionic groups, suitably phosphate, phosphonate, sulphate, sulphonate or carboxylic acid groups and they are preferably phosphate groups. If present, the anionic groups can be native or introduced by means of chemical treatment in conventional manner; native potato starch contains a substantial amount of covalently bound phosphate monoester groups. In amphoteric polysaccharides,
30 cationic groups are preferably present in a predominant amount, i.e. the polysaccharide suitably has an overall cationic charge. The polysaccharide may be selected from any polysaccharide known in the art including starch, guar gum, cellulose, chitins, chitosans, glycans, galactans, glucans, xanthan gums, pectin, mannan, dextrin, preferably, starch and guar gum. Examples of suitable starches include potato, corn, wheat, tapioca, rice, waxy
35 maize, etc..

The aromatic group of the polysaccharide can be attached to a heteroatom like oxygen present in the polysaccharide. Preferably, the aromatic group is attached to a

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heteroatom, e.g. nitrogen or oxygen, the heteroatom optionally being charged, for example when it is a nitrogen. The aromatic group can also be attached to a group comprising a heteroatom, e.g. amide, ester or ether, which groups can be attached to the polysaccharide backbone(main-chain), for example via a chain of atoms. Example of suitable aromatic groups and groups comprising an aromatic group include aryl and aralkyl groups, e.g. phenyl, phenylene, naphthyl, phenylene, xylylene, benzyl and phenylethyl; nitrogen-containing aromatic (aryl) groups, e.g. pyridinium and quinolinium, as well as derivatives of these groups where one or more substituents attached to said aromatic groups can be selected from hydroxyl, halides, e.g. chloride, nitro, and hydrocarbon groups having from 1 to 4 carbon atoms.

Particularly suitable polysaccharides include those comprising the general structural formula (I):



wherein P is a residue of a polysaccharide; A is a group attaching N to the polysaccharide residue, suitably a chain of atoms comprising C and H atoms, and optionally O and/or N atoms, usually an alkylene group with from 2 to 18 and suitably 2 to 8 carbon atoms, optionally interrupted or substituted by one or more heteroatoms, e.g. O or N, e.g. an alkyleneoxy group or hydroxy propylene group ($\text{---CH}_2\text{---CH(OH)---CH}_2\text{---}$); R_1 and R_2 are each H or, preferably, a hydrocarbon group, suitably alkyl, having from 1 to 3 carbon atoms, suitably 1 or 2 carbon atoms; R_3 is suitably an aromatic hydrocarbon group including aralkyl groups, e.g. benzyl and phenylethyl groups; n is an integer from about 2 to about 300,000, suitably from 5 to 200,000 and preferably from 6 to 125,000 or, alternatively, R_1 , R_2 and R_3 together with N form a aromatic group containing from 5 to 12 carbon atoms; and X^- is an anionic counterion, usually a halide like chloride.

The aromatic group modified cationic or amphoteric polysaccharide can have a degree of substitution varying over a wide range; the degree of cationic substitution (DS_C) can be from 0,01 to 0,5, suitably from 0,02 to 0,3, preferably from 0,025 to 0,2, the degree of aromatic substitution (DS_Ar) can be from from 0,01 to 0,5, suitably from 0,02 to 0,3, preferably from 0,025 to 0,2, and the degree of anionic substitution (DS_A) can be from 0 to 0,2, suitably from 0 to 0,1, preferably from 0 to 0,05.

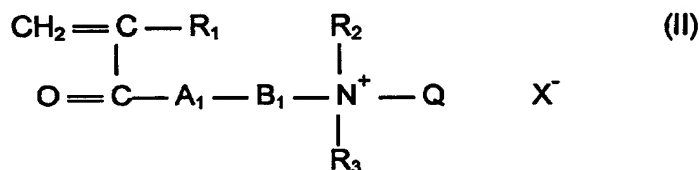
The polysaccharides can be prepared by subjecting a polysaccharide to cationic and aromatic modification in known manner using one or more agents containing a cationic group and/or a aromatic group, for example by reacting the agent with the polysaccharide in the presence of an alkaline substance such as an alkali metal or alkaline earth metal

hydroxide. The polysaccharide to be subjected to cationic and aromatic modification can be non-ionic, anionic, amphoteric or cationic. Suitable modifying agents include non-ionic agents such as, for example aralkyl halides, e.g. benzyl chloride and benzyl bromide; the reaction products of epichlorohydrin and dialkylamines having at least one substituent comprising an aromatic group as defined above, including 3-dialkylamino-1,2-epoxypropanes; and cationic agents such as, for example, the reaction product of epichlorohydrin and tertiary amines having at least one substituent comprising an aromatic group as defined above, including alkaryldialkylamines, e.g. dimethylbenzylamine; arylamines, e.g. pyridine and quinoline. Suitable cationic agents of this type include 2,3-epoxypropyl trialkylammonium halides and halohydroxypropyl trialkylammonium halides, e.g. N-(3-chloro-2-hydroxypropyl)-N-(hydrophobic alkyl)-N,N-di(lower alkyl)ammonium chloride and N-glycidyl-N-(hydrophobic alkyl)-N,N-di(lower alkyl)ammonium chloride where the aromatic group is as defined above, notably octyl, decyl and dodecyl, and the lower alkyl is methyl or ethyl; and halohydroxypropyl-N,N-dialkyl-N-alkarylammonium halides and N-glycidyl-N-(alkaryl)-N,N-dialkylammonium chloride, e.g. N-(3-chloro-2-hydroxypropyl)-N-(alkaryl)-N,N-di(lower alkyl)ammonium chloride where the alkaryl and lower alkyl groups are as defined above, particularly N-(3-chloro-2-hydroxypropyl)-N-benzyl-N,N-dimethylammonium chloride; and N-(3-chloro-2-hydroxypropyl) pyridinium chloride. Generally, when using a non-ionic aromatic agent, the polysaccharide is suitably rendered cationic by using any of the cationic agents known in the art before or after the hydrophobic modification. Examples of suitable cationic and/or aromatic modifying agents, aromatic group modified polysaccharides and methods for their preparation include those described in U.S. Patent Nos. 4,687,519 and 5,463,127; International Patent Application WO 94/24169, European Patent Application No. 189 935; and S.P. Patel, R.G. Patel and V.S. Patel, Starch/Stärke, 41(1989), No. 5, pp. 192-196, the teachings of which are hereby incorporated herein by reference.

Polymer (b) may also be a synthetic polymer, suitably cationic, selected from homopolymers and copolymers prepared from one or more monomers comprising at least one monomer having an aromatic group, suitably an ethylenically unsaturated monomer. The synthetic polymer may be branched linear or branched. The aromatic group of the synthetic polymer can be present in the polymer backbone or, preferably, it can be a pendant group attached to or extending from the polymer backbone or be present in a pendent group that is attached to or extending from polymer backbone. Suitable aromatic (aryl) groups include those comprising a phenyl group, optionally substituted, a phenylene group, optionally substituted, and a naphthyl group, optionally substituted, for example groups having the general formulae $-C_6H_5$, $-C_6H_4-$, $-C_6H_3-$, and $-C_6H_2-$, e.g. in the form of phenylene ($-C_6H_4-$), xylylene ($-CH_2-C_6H_4-CH_2-$), phenyl ($-C_6H_5$), benzyl ($-CH_2-C_6H_5$),

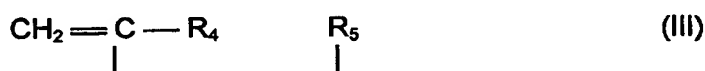
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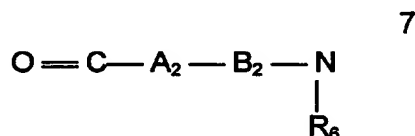
phenethyl ($-\text{CH}_2\text{CH}_2-\text{C}_6\text{H}_5$), and substituted phenyl (for example $-\text{C}_6\text{H}_4-\text{Y}$, $-\text{C}_6\text{H}_3\text{Y}_2$, and $-\text{C}_6\text{H}_2\text{Y}_3$) where one or more substituents (Y) attached to the phenyl ring can be selected from hydroxyl, halides, e.g. chloride, nitro, and hydrocarbon groups having from 1 to 4 carbon atoms. Polymer (b) is preferably a vinyl addition polymer. The term "vinyl addition polymer" as used herein, refers to a polymer prepared by addition polymerisation polymerization of one or more vinyl monomers or ethylenically unsaturated monomers which include, for example, acrylamide-based and acrylate-based monomers. Suitable synthetic polymers include cationic vinyl addition polymers obtained by polymerizing a cationic monomer or a monomer mixture comprising a cationic monomer represented by the general formula (II):



wherein R_1 is H or CH_3 ; R_2 and R_3 are each or, preferably, an alkyl group having from 1 to 3 carbon atoms, usually 1 to 2 carbon atoms; A_1 is O or NH; B_1 is an alkylene group having from 2 to 8 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group; Q is a substituent containing an aromatic group, suitably a phenyl or substituted phenyl group, which can be attached to the nitrogen by means of an alkylene group usually having from 1 to 3 carbon atoms, suitably 1 to 2 carbon atoms, and preferably Q is a benzyl group ($-\text{CH}_2-\text{C}_6\text{H}_5$); and X^- is an anionic counterion, usually a halide like chloride. Examples of suitable monomers represented by the general formula (II) include quaternary monomers obtained by treating dialkylaminoalkyl (meth)acrylates, e.g. dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate and dimethylaminohydroxypropyl (meth)acrylate, and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide, and diethylaminopropyl (meth)acrylamide, with benzyl chloride. Preferred cationic monomers of the general formula (II) include dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylmethacrylate benzyl chloride quaternary salt.

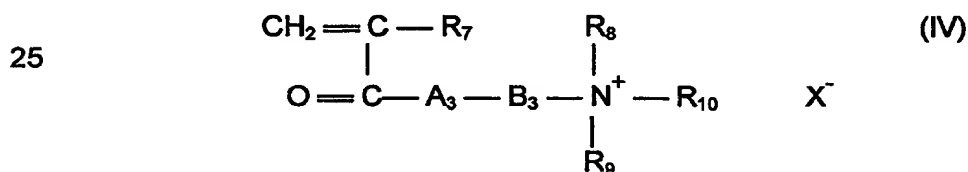
The synthetic cationic polymer can be a homopolymer prepared from a cationic monomer having an aromatic group or a copolymer prepared from a monomer mixture comprising a cationic monomer having an aromatic group and one or more copolymerizable monomers. Suitable copolymerizable non-ionic monomers include monomers represented by the general formula (III):





- 5 wherein R_4 is H or CH_3 ; R_5 and R_6 are each H or a hydrocarbon group, suitably alkyl, having from 1 to 6, suitably from 1 to 4 and usually from 1 to 2 carbon atoms; A_2 is O or NH; B_2 is an alkylene group of from 2 to 8 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group or, alternatively, A and B are both nothing whereby there is a single bond between C and N ($\text{O}=\text{C}-\text{NR}_5\text{R}_6$). Examples of suitable copolymerizable
- 10 monomers of this type include (meth)acrylamide; acrylamide-based monomers like N-alkyl (meth)acrylamides and N,N-dialkyl (meth)acrylamides, e.g. N-n-propylacrylamide, N-isopropyl (meth)acrylamide, N-n-butyl (meth)acrylamide, N-isobutyl (meth)acrylamide and N-t-butyl (meth)acrylamide; and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide and diethylaminopropyl (meth)acrylamide; acrylate-based monomers like dialkyl-
- 15 aminoalkyl (meth)acrylates, e.g. dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, t-butylaminoethyl (meth)acrylate and dimethylaminohydroxypropyl acrylate; and vinylamides, e.g. N-vinylformamide and N-vinylacetamide. Preferred copolymerizable non-ionic monomers include acrylamide and methacrylamide, i.e. (meth)acrylamide, and the
- 20 main polymer is preferably an acrylamide-based polymer.

Suitable copolymerizable cationic monomers include the monomers represented by the general formula (IV):



- 30 wherein R_7 is H or CH_3 ; R_8 , R_9 and R_{10} are each H or, preferably, a hydrocarbon group, suitably alkyl, having from 1 to 3 carbon atoms, usually 1 to 2 carbon atoms; A_3 is O or NH; B_3 is an alkylene group of from 2 to 4 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group, and X^- is an anionic counterion, usually methylsulphate or a halide like chloride. Examples of suitable cationic copolymerizable monomers include acid addition
- 35 salts and quaternary ammonium salts of the dialkylaminoalkyl (meth)acrylates and dialkylaminoalkyl (meth)acrylamides mentioned above, usually prepared using acids like HCl, H_2SO_4 , etc., or quaternizing agents like methyl chloride, dimethyl sulphate, etc.; and diallyldimethylammonium chloride. Preferred copolymerizable cationic monomers include dimethylaminoethyl (meth)acrylate methyl chloride quaternary salt and diallyldimethyl-
- 40 ammonium chloride. Copolymerizable anionic monomers like acrylic acid, methacrylic acid,

various sulfonated vinyl addition monomers, etc. can also be employed and, preferably, in minor amounts.

The synthetic cationic polymer can be prepared from a monomer mixture generally comprising from 1 to 99 mole%, suitably from 2 to 50 mole% and preferably from 5 to 20 mole% of cationic monomer having an aromatic group, preferably represented by the general formula (II), and from 99 to 1 mole%, suitably from 98 to 50 mole%, and preferably from 95 to 80 mole% of other copolymerizable monomers which preferably comprises acrylamide or methacrylamide ((meth)acrylamide), the monomer mixture suitably comprising from 98 to 50 mole% and preferably from 95 to 80 mole% of (meth)acrylamide, the sum of percentages being 100.

The synthetic polymer can also be selected from polymers prepared by condensation reaction of one or more monomers containing an aromatic group. Examples of such monomers include toluene diisocyanates, bisphenol A, phthalic acid, phthalic anhydride, etc., which can be used in the preparation of cationic polyurethanes, cationic polyamideamines, etc.

Alternatively, or additionally, the synthetic polymer can be a polymer subjected to aromatic modification using an agent containing an aromatic group. Suitable modifying agents of this type include benzyl chloride, benzyl bromide, N-(3-chloro-2-hydroxypropyl)-N-benzyl-N,N-dimethylammonium chloride, and N-(3-chloro-2-hydroxypropyl) pyridinium chloride. Suitable polymers for such an aromatic modification include vinyl addition polymers. If the polymer contains a tertiary nitrogen which can be quaternized by the modifying agent, the use of such agents usually results in that the polymer is rendered cationic. Alternatively, the polymer to be subjected to aromatic modification can be cationic, for example a cationic vinyl addition polymer.

Usually the charge density of the synthetic polymer is within the range of from 0.1 to 6.0 meqv/g of dry polymer, suitably from 0.2 to 4.0 and preferably from 0.5 to 3.0. The weight average molecular weight of the synthetic polymers is usually at least about 500,000, suitably above about 1,000,000 and preferably above about 2,000,000. The upper limit is not critical; it can be about 50,000,000, usually 30,000,000 and suitably 25,000,000.

Examples of suitable synthetic polymers include those described in U.S. Patent Nos. 5,169,540; 5,708,071; and European Patent Applications 183,466; 525,751 and 805,234; the disclosures of which are hereby incorporated herein by reference. When being added to the stock, the synthetic polymer is suitably in liquid form, e.g. in the form of an aqueous solution or dispersion.

Polymer (a) and polymer (b) may be in any state such as, for example, in solid form, e.g. powders, in liquid form, e.g. solutions, emulsions, dispersions, including salt dispersions, etc.

The process according to the present invention comprises adding to a suspension containing cellulosic fibres an anionic or cationic aqueous sizing dispersion, i.e. the dispersing and/or stabilising agents present have an overall anionic or cationic charge, respectively. By anionic or cationic aqueous sizing dispersion is meant that the dispersant
5 has an overall anionic or cationic charge. The dispersant can include any agent facilitating the formation of a dispersion or emulsion such as dispersing and/or stabilising agents exemplified by polyelectrolytes, surfactants and electrolytes. Anionic aqueous sizing dispersions may comprise cationic compounds, i.e. cationic polyelectrolytes (cationic or amphoteric polyelectrolytes with overall cationic charge) and/or cationic surfactants and/or
10 any other cationic compound known to the skilled person provided that the overall charge of the dispersant (system) is anionic. Cationic aqueous sizing dispersions, on the other hand, can comprise anionic compounds, i.e. anionic polyelectrolytes (anionic or amphoteric polyelectrolytes with an overall anionic charge) and/or anionic surfactants and/or any other anionic compound known to the skilled person provided that the overall charge of the
15 dispersant is anionic. According to one preferred embodiment the sizing dispersion is cationic. According to another preferred embodiment the sizing dispersion is anionic. The anionic or cationic charge of the sizing dispersion can be determined by means of a ZetaMaster S version PCS. Suitably, the sizing dispersion also contains additional dispersing agents and/or stabilising agents known in the art.

20 The anionic or cationic sizing dispersion added to the suspension suitably can have a sizing agent content from 0.1 to 50 % by weight based on total dispersion/emulsion, suitably over 20% by weight. Dispersions comprising ketene dimer sizing agents may have ketene dimer contents from 5 up to 50 % by weight based on total dispersion, preferably from 10 up to 35% by weight. Dispersions, or emulsions, comprising acid anhydride sizing
25 agents may have acid anhydride contents from 0.1 up to 30 % by weight based on total dispersion/emulsion, suitably from 1 up to 20 % by weight. Dispersions containing non-cellulose reactive sizing agents suitably have sizing agent contents from 5 up to 50 % by weight, preferably from 10 up to 35 % by weight.

The amount of sizing agent added to the suspension containing cellulosic
30 fibres can be from 0.01 to 5 % by weight, suitably from 0.05 to 1.0 % by weight, based on dry weight of cellulosic fibres and optional fillers, where the dosage is dependent on the quality of the pulp or paper to be sized, the sizing agent and the level of sizing.

The anionic or cationic sizing dispersion can comprise a further polymer (c) containing at least one aromatic group and can include any of the polymers (a) and (b) as
35 defined above in amounts varying within wide limits depending on, inter alia, the molecular weight of polymer (c), ionic substitution of polymer (c), desired overall charge of the dispersion and sizing agent(s) used. Polymer (c) may be present in the dispersion in an

amount of up to 40% by weight, suitably from 0.1 up to 35% by weight and preferably from 0.3 up to 30% by weight based on the sizing agent.

The process for sizing paper according to the present invention comprises adding to a suspension containing cellulosic fibres an anionic or cationic aqueous sizing dispersion, and a sizing promoter comprising an anionic polymer (a) containing at least one aromatic group. Suitably polymer (a) includes lignosulphonates, condensated naphthalene sulphonates and/or polystyrene sulphonates or mixtures thereof. The sizing promoter comprising a polymer (a) may contain cationic and/or amphoteric polymers such as polysaccharides (starches, guar gums) and synthetic polymers, i.e. vinyl addition polymers. Further anionic compound may also be comprised in the sizing promoter, for example anionic microparticulate materials such as anionic inorganic particles. Preferably, polymer (a) forms part of a drainage and retention system comprising two or more components.

One preferred embodiment of the present invention comprises adding to a suspension containing cellulosic fibres an anionic or cationic aqueous sizing dispersion, and a sizing promoter comprising an anionic polymer (a) and a polymer (b), wherein polymers (a) contains at least one aromatic group and (b) contains at least one aromatic group. The polymers (a), (b) can be any of the polymers mentioned above. Suitably, polymer (b) is a cationic or amphoteric polymer, i.e. a polymer with an overall cationic charge. The sizing promoter comprising a polymer (a) and a polymer (b) can be referred to as a drainage and retention system. The sizing promoter comprising a polymer (a) and (b), which suitably are of opposite charge, may further comprise components such as anionic microparticulate materials, e.g. anionic organic particles and anionic inorganic particles, water-soluble anionic vinyl addition polymers, low molecular weight cationic organic polymers, aluminium compounds, and combinations thereof.

Yet another preferred embodiment of the present invention comprises adding to a suspension containing cellulosic fibres an anionic or cationic sizing dispersion, and a sizing promoter comprising an anionic polymer (a) containing at least one aromatic group, preferably polymer (a) contains at least one sulphonate group, most preferably polymer (a) is selected from condensated naphthalene sulphonates, polystyrene sulphonates and lignosulphonates, and a polymer (b) containing at least one aromatic group selected from cationic or amphoteric polysaccharides or cationic vinyl addition polymers. Suitably, polymer (b) is selected from the group consisting of cationic or amphoteric polysaccharides.

According to yet another preferred embodiment of the present invention an anionic or cationic sizing dispersion comprising a polymer (c) containing at least one aromatic group and a sizing promoter comprising a polymer (a) and polymer (b) is added to the suspension.

Polymer (a) and polymer (b), or any other components comprised in the sizing promoter may be added separately to the suspension or together/simultaneously to the

suspension at essentially the same position. Suitably, polymer (b) or any other component comprised in the sizing promoter having an overall cationic charge (cationic/amphoteric) is added to the suspension prior to a polymer (a) or any other component having an overall anionic charge. It is further preferred to add a polymer (b) or any other component having an overall cationic charge before a shear stage, which can be selected from pumping, mixing
5 cleaning, etc., and to add a polymer (a) or any other component having an overall anionic charge after the shear stage.

The polymers containing at least one aromatic group, i.e. polymer (a), (b) and (c) may be in any state, e.g. in solid form (powder), in liquid form such as solution, emulsion,
10 dispersion, including salt dispersions. When polymer (a) and optionally polymer (b), forming the sizing promoter, are added to the stock, they are preferably provided in liquid form, e.g. in the form of an aqueous solution or dispersion.

The sizing dispersion optionally comprising polymer (c) and the sizing promoter comprising a polymer (a) and suitably a polymer (b) can be added simultaneously or
15 separately to the cellulosic stock, preferably separately, whereby the polymer (a) and/or (b) or any other component comprised in the sizing promoter and the sizing dispersion may be added in any order to the suspension. Preferably, the sizing dispersion is added subsequent to the addition of the promoter, i.e. subsequent polymer (a) and optionally polymer (b).

Polymer (a) and optionally polymer (b) can be added to the stock in amounts which
20 can vary within wide limits depending on, inter alia, type of furnish, filler content, type of filler, point of addition, salt content, etc. Generally, the sizing promoter, i.e. polymer (a) and/or (b) and/or any other component are added in an amount that give the paper improved sizing properties than is obtained when not adding the sizing promoter. Suitably, polymer (a) or polymer (b) are added to the furnish in an amount of at least 0.001 % by weight up to 10 %
25 based on dry furnish substance. If polymer (b) is a polysaccharide, the polymer is added to the stock in an amount of at least 0.01 %, suitably at least 0.1 % by weight based on dry stock substance, and the upper limit is usually 10 % preferably 2 %. In case polymer (b) are synthetic cationic polymers they are added to the stock in an amount of at least 0.001 %, suitably at least 0.005 % by weight, based on dry stock substance, whereas the upper limit
30 is usually 3 %, preferably 1.5 % by weight. Polymer (a) can be added to the stock in an amount of from 0.005 up to 0.5 % by weight based on dry stock substance, suitably from 0.01 up to 0.2% by weight.

The process of the invention is preferably used in the manufacture of paper from a suspension containing cellulosic fibers, and optional fillers, having a high conductivity.
35 Usually, the conductivity of the stock is at least 0.20 mS/cm, suitably at least 0.5 mS/cm, preferably at least 3.5 mS/cm. Very good sizing results have been observed at conductivity levels above 5.0 mS/cm and even above 7.5 mS/cm. Conductivity can be measured by

- standard equipment such as, for example a WTW LF 539 instrument supplied by Christian Berner. The values referred to above are suitably determined by measuring the conductivity of the cellulosic suspension that is fed into or present in the headbox of the paper machine or, alternatively, by measuring the conductivity of white water obtained by dewatering the suspension. High conductivity levels mean high contents of salts (electrolytes), where the various salts can be based on mono-, di- and multivalent cations like alkali metals, e.g. Na^+ and K^+ , alkaline earths, e.g. Ca^{2+} and Mg^{2+} , aluminium ions, e.g. Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and polyaluminium ions, and mono-, di- and multivalent anions like halides, e.g., Cl^- , sulfates, e.g. SO_4^{2-} and HSO_4^- , carbonates, e.g. CO_3^{2-} and HCO_3^- , silicates and lower organic acids.
- The invention is particularly useful in the manufacture of paper from stocks having high contents of salts of di- and multivalent cations, and usually the cation content is at least 200 ppm, suitably at least 300 ppm and preferably at least 400 ppm. The salts can be derived from the cellulosic fibres and fillers used to form the stock, in particular in integrated mills where a concentrated aqueous fibre suspension from the pulp mill normally is mixed with water to form a dilute suspension suitable for paper manufacture in the paper mill. The salt may also be derived from various additives introduced into the stock, from the fresh water supplied to the process, or be added deliberately, etc. Further, the content of salts is usually higher in processes where white water is extensively recirculated, which may lead to considerable accumulation of salts in the water circulating in the process.
- The present invention further encompasses papermaking processes where white water is extensively recirculated (recycled), i.e. with a high degree of white water closure, for example where from 0 to 30 tons of fresh water are used per ton of dry paper produced, usually less than 20, suitably less than 15, preferably less than 10 and notably less than 5 tons of fresh water per ton of paper. Recirculation of white water obtained in the process suitably comprises mixing the white water with cellulosic fibres and/or optional fillers to form a suspension to be sized; preferably it comprises mixing the white water with a suspension containing cellulosic fibres, and optional fillers, before the suspension enters the forming wire for sizing.
- Further additives which are conventional in papermaking can of course be used in combination with the additives according to the invention, such as, for example, additional dry strength agents, wet strength agents. The cellulosic suspension, or stock, can also contain mineral fillers of conventional types such as, for example, kaolin, china clay, titanium dioxide, gypsum, talc and natural and synthetic calcium carbonates such as chalk, ground marble and precipitated calcium carbonate.
- The process of this invention is used for the production of paper. The term "paper", as used herein, of course include not only paper and the production thereof, but also other sheet or web-like products, such as for example board and paperboard, and the production

thereof. The process can be used in the production of paper from different types of suspensions of cellulose-containing fibres and the suspensions should suitably contain at least 25% by weight and preferably at least 50% by weight of such fibres, based on dry substance. The suspensions can be based on fibres from chemical pulp such as sulphate, sulphite and organosolv pulps, mechanical pulp such as thermomechanical pulp, chemo-thermomechanical pulp, refiner pulp and groundwood pulp, from both hardwood and softwood, and can also be based on recycled fibres, optionally from de-inked pulps, and mixtures thereof. The invention is particularly useful in the manufacture of paper from suspensions based on pulps comprising recycled fibres and de-inked pulp, and the content of cellulosic fibres of such origin can be up to 100%, suitably from 20 to 100%.

The invention is further illustrated in the following Examples which, however, are not intended to limit the same. Parts and % relate to parts by weight and % by weight, respectively, unless otherwise stated.

15 Example 1

The sizing performance of the process was evaluated by using the cobb 60 test.

An anionic sizing dispersion was prepared containing alkyl ketene dimer, condensated naphthalene sulphonate and di(hydrogenated tallow) dimethylammonium chloride. The sizing dispersion had an AKD content of 30% and contained 4% of di(hydrogenated tallow) dimethylammonium chloride and 6% of condensated naphthalene sulphonate based on AKD. The sizing dispersion was added to the stock in an amount of 5 kg AKD/tonne dry stock.

Condensated naphthalene sulphonate (available under the trade name Tamol ®) comprised in the sizing promoter was added to the furnish (test 1). In test 2 the sizing promoter comprised additionally a cationic starch with a cationic substitution DS of 0.065 regarding nitrogen containing benzyl groups. Moreover, additional components comprised in the sizing promoter were added to the stock where appropriate and indicated by table 1 including cationic starch without aromatic groups with a cationic substitution of 0.065 and anionic inorganic silica particles provided as a sol.

The furnish used was based on 80 % by weight of bleached birch/pine (60/40) sulphate pulp and 20 % by weight of CaCO₃ refined to 200 CSF and containing 0.3 g/litre stock Na₂SO₄, having a conductivity of 461 µS/cm and a pH of 8,1.

Table 1

	anionic sizing dispersion/ [kg sizing	cationic starch containing	cationic starch (without
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	agent/tonne dry stock]	aromatic groups/[kg /tonne dry stock]	aromatic groups)/[kg starch/tonne dry stock]
test 1 (ref.)	0,5	0	10
test 2	0,5	0	10
test 3	0,5	10	0

	cond. naphtalene sulphonate/ [kg cond./tonne dry stock]	anionic silica particles/[kg silica part./tonne dry stock]	cobb 60/[g/m ²]
test 1 (ref.)	0	1	45,2
test 2	1	0	26,5
test 3	1	0	29,3

Example 2

- The sizing performance of the process was evaluated (cobb 60 test) using the same
- 5 anionic sizing dispersion and the same sizing promoters as in example 1, however, calcium chloride was added to the stock to adjust the conductivity to 5000 $\mu\text{S/cm}$.

Table 2

	anionic sizing dispersion/ [kg sizing agent/tonne dry stock]	cationic starch containing aromatic groups /[kg /tonne dry stock]	cationic starch (without aromatic groups)/[kg starch/tonne dry stock]
test 1 (ref.)	0,5	10	0
test 2	0,5	10	0

	cond. naphtalene sulphonate/	anionic silica particles/[kg silica	cobb 60/[g/m ²]
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	[kg cond./tonne dry stock]	part./tonne dry stock]	
test 1 (ref.)	0	1	75
test 2	1	0	27,8

Example 3

- 5 The sizing performance was evaluated using a cationic sizing dispersion which contained 15 % of alkyl ketene dimer, 2 % of cationic starch and 0.6% of sodium lignosulphonte, based on AKD. The components and added amount of components comprised in the sizing promoter, apparent from table 3, included condensated naphtalene sulphonate, cationic starch without aromatic groups having a DS of 0.065, cationic starch containing
- 10 aromatic groups having a DS of 0.065 and anionic inorganic silica particles provided as a sol. The stock used was that of example 2 having a pH of 8.1 and a conductivity of 5000 $\mu\text{S}/\text{cm}$ by the addition of calcium chloride to the stock.

Table 3

	cationic sizing dispersion/ [kg sizing agent/tonne dry stock]	cationic starch containing aromatic groups /[kg /tonne dry stock]	cationic starch (without aromatic groups)/[kg starch/tonne dry stock]
test 1 (ref.)	0,5	0	10
test 2	0,5	0	10
test 3	0,5	10	0

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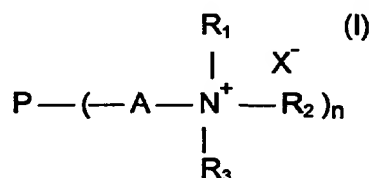
	cond. naphtalene sulphonate/ [kg cond./tonne dry stock]	anionic silica particles/[kg silica part./tonne dry stock]	cobb 60/[g/m ²]
test 1 (ref.)	0	1	55

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test 2	1	0	34
test 3	1	0	27,8

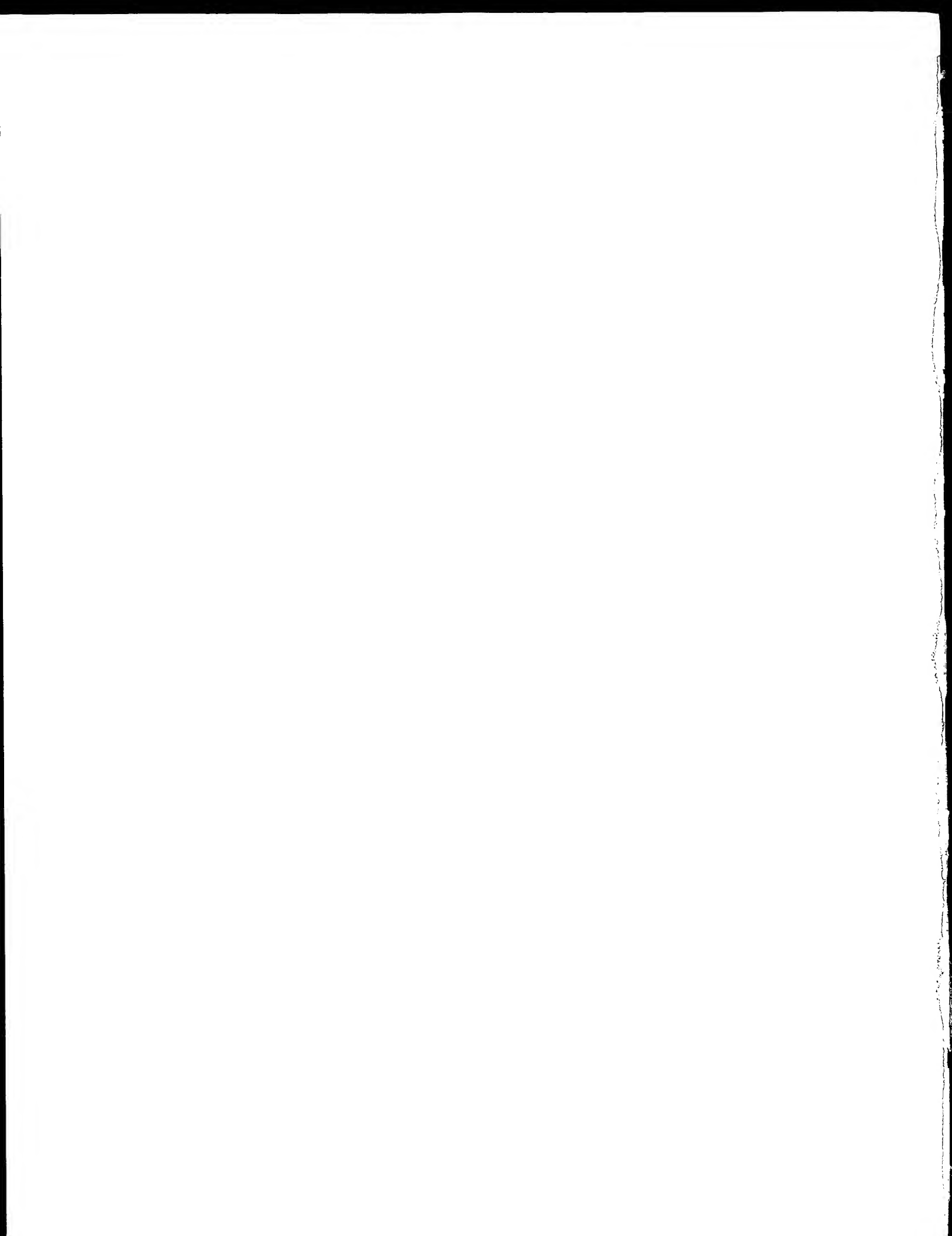
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Claims

1. A process for sizing paper comprising adding to a suspension containing cellulosic fibres an anionic or cationic sizing dispersion, and a sizing promoter, c h a r a c t e r i s e d in that the sizing promoter comprises an anionic polymer (a) containing at least one aromatic group.
2. A process for sizing paper comprising adding to a suspension containing cellulosic fibres an anionic or cationic sizing dispersion, and a sizing promoter, c h a r a c t e r i s e d in that the sizing promoter comprises an anionic polymer (a) containing at least one aromatic group and a polymer (b) containing at least one aromatic group selected from cationic or amphoteric polysaccharides or cationic vinyl addition polymers.
3. A process according to claim 2, c h a r a c t e r i s e d in that polymer (b) is selected from the group consisting of cationic and amphoteric polysaccharides.
4. A process according to claim 2 and 3, c h a r a c t e r i s e d in that polymer (b) is a cationic or amphoteric polysaccharide having the general structural formula (I):



wherein P is a residue of a polysaccharide; A is a chain of atoms comprising C and H atoms attaching N to the polysaccharide residue, R₁ and R₂ are each H or a hydrocarbon group, R₃ is an aromatic hydrocarbon group, n is an integer from 2 up to 300000, and X⁻ is an anionic counter ion.

5. A process according to any of the preceding claims, c h a r a c t e r i s e d in that polymer (a) contains at least one sulphonate group.
6. A process according to any of the preceding claims c h a r a c t e r i s e d in that polymer (a) is selected from condensed naphthalene sulphonates, polystyrene sulphonates and lignosulphonates.
7. A process according to any of the claims, c h a r a c t e r i s e d in that the anionic or cationic sizing dispersion comprises a polymer (c) containing at least one aromatic group.
8. A process according to any of the preceding claims, c h a r a c t e r i s e d in that the sizing dispersion comprises a cellulose-reactive sizing agent.
9. A process according to any of the preceding claims, c h a r a c t e r i s e d in that the sizing dispersion is cationic.
10. A process according to any of the preceding claims, c h a r a c t e r i s e d in that the sizing dispersion is anionic.



18

Abstract

The present invention refers to a process for sizing paper comprising adding to a suspension containing cellulosic fibres an anionic or cationic sizing dispersion, and a sizing promoter, wherein the sizing promoter comprises an anionic polymer (a) containing
5 at least one aromatic group and optionally a polymer (b) containing at least one aromatic group.

